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**Transmittal of Provisional Application**

Mail Stop Provisional Patent Application  
Commissioner for Patents  
P.O. Box 1450  
Alexandria, VA 22313-1450

Inventor(s): Kehju Kamiyama, Yamagata, Japan

Title: DECORATIVE PROTECTIVE FILM



1. ☒ Enclosed is the above-identical new provisional application for patent under 35 USC § 111(b)(1). It includes:  
    32 Pages of Text  
    1 Sheets of Drawings
2. ☐ Enclosed is an executed Assignment to 3M Innovative Properties Company and a completed Assignment Recordation Cover Sheet.
3. ☐ This invention was made under a contract with an agency of the U.S. Government:  
    Agency: \_\_\_\_\_  
    Contract No. \_\_\_\_\_
4. ☒ Correspondence Address: James V. Lilly  
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5. ☒ Please charge the \$160.00 filing fee under 37 CFR § 1.16(k) to Deposit Account No. 13-3723. One copy of this sheet marked duplicate is also enclosed.
6. ☒ Please charge to Deposit Account No. 13-3723 any fees under 37 CFR §§ 1.16 and 1.17, which may be required to file and during the entire pendency of this application. This authorization includes the fee for any necessary extension of time under 37 CFR § 1.136(a). To the extent any such extension should become necessary, it is hereby requested.
7. ☒ Enclosed is a return receipt postcard.

Respectfully submitted,

October 28, 2003  
Date

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Pursuant to 37 CFR § 1.10, this application and the documents and fees listed on this transmittal letter are being deposited on the date indicated below with the United States Postal Service "Express Mail Post Office to Addressee" service addressed to: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450

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## 10

The present invention relates to a decorative protective film, and particularly to a decorative protective film that is adhered to a surface of an article having a three-dimensional surface, such furniture, an outside or inside surface of a building, a vending machine, a sign, in order to protect and decorate the surface of the article.

## 15

A decorative protective film is a thermoplastic sheet having a decorative image on one surface and an adhesive layer on the other surface. It is commonly used to provide decorative images on an article having a two or three-dimensional surface, such as an outside or inside surface of a building or a vending machine. The decorative protective film is generally adhered on a surface of an article by the following two methods:

20

(1) A decorative protective film is positioned on the surface of an article, heated in place to a given temperature, generally 40 to 60°C, and is adhered to the article under heat and pressure.

(2) A decorative protective film is adhered to an article by a molding method, such as vacuum molding under heating and the like.

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Typically, the decorative protective film is made of a material suitable for use in the above methods. Typically such a decorative protective film contains poly(vinyl chloride). Poly(vinyl chloride) has good heat moldability and good protective properties such as wear resistance, chemical resistance and the like. However, in recent times, there have been concerns over the disposal of poly(vinyl chloride) and issues of recyclability.

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Polyolefins or polyester sheets have been proposed as replacements for the poly(vinyl chloride) in such sheets. Japanese Kokai Publications describing decorative protective films

are described in Japanese Kokai Publication No. 48014/1996 and Japanese Kokai Publication No. 2000-94596. Other decorative films are also disclosed in WO 02/081231.

One issue with polyolefins is that they generally have softening temperatures that are too high - more than 100°C. Many polyesters have a glass transition temperature of 60 to 85°C. It can be difficult to apply sheets having softening temperatures above 60°C using many hand-held hot air blowers and the second method of application described above. Furthermore, such decorative sheets are exposed to continuous loads, scrapes, abrasion and decorative sheets can be torn if impacted by a sharp or heavy objects.

What is needed is a decorative film having low or no poly(vinyl chloride) content having the properties of easy conformability and adhesion at 60 to 85°C during in-situ application to a three dimensional article, and further having impact, tear and abrasion resistance.

#### Brief Description

The presents invention comprises a decorative protective film which can be adhered and conformed onto a two or three-dimensional surface of an article to form an article, even when such an application is conducted in situ at a temperature in the range of 40 to 60°C. Advantageously, the decorative protective film of the present invention does not utilize poly(vinyl chloride), and further has a good impact resistance.

In one embodiment of the invention, the decorative protective film comprises a toughening layer having a first major surface and a second major surface; and a protective layer having a first major surface and a second major surface, wherein the second surface of the protective layer is bonded to the first surface of the toughening layer; and an adhesive layer having a first major surface and a second major surface, wherein the first surface of the adhesive layer is bonded to the second surface of the toughening layer, wherein the toughening layer comprises a thermoplastic polyurethane polymer having a glass transition temperature of from -50°C to 0°C, and wherein the protective layer comprises an amorphous thermoplastic polyester resin, wherein the protective layer has a tensile modulus of 400 to 1300 MPa.

When the protective layer is a layer of amorphous thermoplastic polyester resin, a highly conformable film is obtained. When a toughening layer of polyurethane having a glass transition temperature in the range of -50°C to 0°C is added, a decorative protective film can be obtained having excellent flexibility and conformability, even when the film is heated in situ for operation at a temperature of only 40 to 60°C. In this context, the term "glass transition temperature" (T<sub>g</sub>) is defined as a peak temperature determined by a differential scanning calorimeter at a scan rate of 5°C / min. and a frequency of 62.8 rad/sec. If the sample is thermally aged, the glass transition temperature can appear as a small endothermic peak in the thermogram (a plot of heat vs. temperature or time). If the sample is not thermally aged (contains free volume), then the glass transition temperature can be indicated by a step in the thermogram plot.

Surprisingly, it has been determined that the combination of a protective layer and a toughening layer provides a decorative protective layer having very good impact and mar resistance over the longer term without sacrificing conformability at mild application temperatures such as when a hot air blower is used, and without sacrificing appearance. Furthermore, they have done this without including poly(vinyl chloride) as a resin into the decorative protective material of the invention.

In a further embodiment of the invention the decorative protective film comprises a toughening layer; a protective layer bonded to a first surface of the toughening layer; and an adhesive layer bonded to a second surface of the toughening layer; wherein the toughening layer comprises a thermoplastic polyurethane polymer having a glass transition temperature of from -50°C to 0°C, and wherein the protective layer comprises an amorphous thermoplastic polyester resin, and wherein the protective layer has a tensile modulus of 400 to 1300 MPa.

In a further embodiment of the invention, the toughening layer comprises a pigment.

In a further embodiment of the invention, the first surface of the protective layer is decorated by a method selected from the group consisting of embossing, printing, and a combination of printing and embossing.

In a further embodiment of the invention, the decorative protective film comprises a decorated interface between the protective layer and the toughening layer. The decorated

interface can be produced by printing the second surface of the protective layer or printing or otherwise decorating the first surface of the toughening layer.

In a further embodiment, the invention is a decorated article comprising a protective layer that comprises an amorphous thermoplastic polyester resin having a glass transition temperature of 20 to 60°C and tensile modulus of 400-1300 MPa; a toughening layer that comprises a polyurethane resin having a glass transition from -50°C to 0°C, the protective layer being bonded to the toughening layer; an adhesive layer bonded to a second surface of the toughening layer to define a decorative film; and an article to which the decorative film is attached. The decorative protective film is conformed to a major surface of the article. The toughening layer of the decorated article may be pigmented.

In a further embodiment, the invention is a method of preparing a protective decorative film, comprising the steps of providing a protective layer, the protective layer comprising a layer of thermoplastic amorphous polyester having a tensile modulus of 400-1300 MPa; applying a toughening layer to a major surface of the protective layer, wherein the toughening layer comprises a polyurethane resin having a glass transition temperature of -50° to 0°C; and applying an adhesive layer to the second surface of the toughening layer.

In a further embodiment, the step of applying a toughening layer to the protective layer comprises coating the toughening layer onto the major surface of the protective layer.

In a further embodiment, the step of applying a toughening layer to the protective layer comprises laminating a free surface of the toughening layer to the major surface of the protective layer.

In further embodiments the method of preparing a decorative protective film comprises one or more of the following steps: decorating the first surface of the protective layer, printing the toughening layer, printing the second surface of the protective layer.

Decorating the first surface of the protective layer can comprise a step selected from the group consisting of printing and embossing.

In a further embodiment, the invention is a method of preparing a protected article comprising the steps of: providing a decorative protective film comprising a protective layer having a first surface and a second surface, wherein the protective layer comprises an amorphous thermoplastic polyester resin, and wherein the protective layer has a tensile

modulus of from 400 to 1300 MPa, wherein the decorative protective film comprises a toughening layer having a first surface and a second surface, wherein the toughening layer comprises a polyurethane resin having a glass transition temperature from -50°C to 0°C, and wherein the second surface of the protective layer is bonded to the first surface of the protective layer, and wherein the decorative protective film comprises an adhesive layer having a first surface and a second surface, wherein the first surface of the adhesive layer is bonded to the second surface of the toughening layer; applying the second surface of the adhesive layer to an article; heating the decorative protective film; and conforming the decorative film to the article.

In a further embodiment, the invention is a method of preparing a protected article comprising the steps of: providing a film; applying an adhesive to an article to form an adhesive coated article; applying the film to the adhesive coated article, heating the film, and conforming the film to the adhesive coated article.

In further embodiments, the film provided for application to the adhesive article comprises a protective layer having a first surface and a second surface, wherein the protective layer comprises an amorphous thermoplastic polyester resin, wherein the protective layer has a tensile modulus of from 400 to 1300 MPa; and a toughening layer having a first surface and a second surface, wherein the toughening layer comprises a polyurethane resin having a glass transition from -50°C to 0°C, wherein the second surface of the protective layer is bonded to the first surface of the toughening layer and wherein applying the film to the adhesive coated article comprises the step of applying the second surface of the toughening layer to the adhesive coated article.

#### Brief Description of the Drawings

Fig. 1 is a schematic cross sectional view of an embodiment of the decorative protective film of the present invention.

Fig. 2 is a schematic cross-sectional view of an embodiment of the decorative protective film of the invention having an embossed surface pattern and printed indicia.



## Detailed Description of Preferred Embodiments

### Decorative protective film

One example of the decorative protective film of the present invention, as shown in Fig. 1, comprises a protective layer 10 and a toughening layer 20, an adhesive layer 30 and an optional liner 40. As can be seen, protective layer 10 is in interfacial contact with first surface 50 of toughening layer 20. As can also be, adhesive layer 30 is in interfacial contact with second surface 60 of toughening layer 20. Adhesive layer 30 is in interfacial contact with a second surface 70 of adhesive layer 40. If the adhesive layer 40 is tacky at room temperature, e.g., when it comprises a pressure sensitive adhesive, then an optional release liner 40 may be disposed on the adhesive layer. However, if the adhesive layer is not tacky at room temperature, for example when it is an activatable adhesive layer such as a hot-melt adhesive layer, then a release liner may not be necessary.

Other types of activatable adhesive layer could include (but are not limited to) solvent-activated such as organic solvent-activated or water-activated adhesive layers, heat-activated adhesive layers (wherein an adhesive layer is heated and changes irreversibly from a non-tacky adhesive layer to a tacky adhesive layer), a light activated adhesive layer (wherein the adhesive layer is irradiated and becomes tacky - either temporarily or permanently) or other type of adhesive layer.

Optionally, a primer layer (not shown) may be located between the protective layer 10 and the toughening layer 20. Additionally, an adhesive prime layer (not shown) may be located between the toughening layer 20 and the adhesive layer 30 to facilitate adhesion between the two. The primer layer may enhance interlayer adhesion, enhance printing ink adhesion to one or more layers, improve print quality or any combination of these. The primer layer may be decorated or otherwise printed.

The adhesive layer 30 is typically a layer of pressure-sensitive adhesive. The adhesive layer 30 can be applied to the toughening layer 20. When a prime layer is present between the protective layer and the toughening layer, the adhesive layer 30 may be applied to the free surface of the prime layer.

When a release liner 40 is employed, it can comprise a base 110 and a release layer 120, where the release layer is for example a silicone release layer. Release liners known in the art typically comprise a base made of paper.

The first (free) surface 80 of the protective layer 10 may be embossed, pressed, cut, ablated, etched, printed, painted calendered or otherwise decorated to give the adhesive sheet a decorated finish as shown in Fig. 2. The decorated finish can comprise finishes or indicia such as letters, patterns, or images. The images can be holograms, photographic color or monochrome images, silhouette images in color, black or white. The finish can be, for example, a wood grain appearance finish, a metallic appearance such as silver or gold. The patterns can be patterns of discreet images such as flowers, animal shapes, diamonds, squares, circles, dots, stripes, chevrons, pear shapes or teardrops, triangles, trapeziums and the like.

The second surface of the protective layer or, alternatively, the first surface of the toughening layer may be decorated to give a decorated interface between the protective layer 10 and the toughening layer 20. The decoration can be achieved by printing, etching, depositing, vapor coating, sputtering, adhering shaped foils, engraving, laser etching, coating and the like. Suitable printing techniques include gravure, inkjet printing (with solvent based inks by either continuous or drop-on-demand inkjet), and lithographic printing. In one embodiment of the invention, the decorated interface is made by printing a repeat pattern by gravure printing organic solvent based inks onto the first surface of the toughening layer.

Figure 2 shows an embodiment of the invention wherein the first surface of the protective layer 10 has been decorated by embossing to provide embossed surface 140. Figure 2 also shows a decorated interface comprising indicia 130 at the interface between protective layer 10 and toughening layer 20. The indicia 130 can be viewed through the transparent protective layer 10.

The decorative protective film may also comprise a surface protection layer (not shown) on the first surface of the protective layer. The surface protection layer can be a stain resistant or dirt resistant layer, a graffiti-resistant layer or other protection layer. The surface protection layer can be coated (for example by gravure printing, knife coating, meter or slot-die coating or by lamination). Examples of a useful surface protection layer include a layer that comprises one or more materials selected from the group consisting of high-surface

energy polymers, ethylene-vinyl alcohol copolymers, ethylene vinyl alcohol acrylic terpolymers, acrylic polymers, fluoropolymers and copolymers of fluorine-containing monomers such as copolymers of polyvinylidene fluoride with acrylic monomers, silicone polymers, polyesters, polyurethanes and copolymers of urethanes, polymers of mixtures of the above monomer types, and polymer blends thereof. Poly(vinylidene) fluoride film is available from Denki Kagaku Kogyo of Tokyo, Japan. The surface protection layer can also be laminated onto the first surface of the protective layer. The surface protection layer in such cases can either be a self-supporting polymer film (such as polyurethane). In such a case, hot lamination is preferable to cold lamination. Or the surface protection layer can be an overlamine wherein the overlamine comprises a polymer film and an adhesive layer. The overlamine further comprises a release liner when the overlamine adhesive layer is a tacky pressure-sensitive heat layer at ambient temperatures.

#### Protective layer

The protective layer useful in the invention may be formed from an amorphous polyester resin composition. The amorphous polyester resin is soft and has good hand and conformability at elevated temperatures, e.g. at 40-60°C. Such temperatures can be obtained by heating with a hot air blower (such as a hair dryer) or the like. The amorphous polyester layer thus can be applied and conformed to curved and complex surface shapes and when softened under heat can be shaped around an article following the contours of the article tightly. The amorphous polyester protective layer has a good heat extension ability that is advantageous for enhancing shape compatibility to curved surface during a hand application of the decorative protective film to an article. Because of the good extensibility, the protective film may be heated and the hot material stretched over the article, tightly conforming the decorative protective film to the article. The amorphous polyester resin has high transparency, and advantageously has a low tendency to whiten when stretched. The protective layer also exhibits good solvent resistance.

Although it is preferred that the protective layer be substantially transparent and colorless, it may be translucent or colored or both for enhancing design properties of the decorative protective film. The protective layer generally has a light transmittance of not less

than 65%, preferably not less than 70%. In the present specification, the "light transmittance" is determined by measuring the light transmittance according to JIS K 7105.

The protective layer has a thickness of preferably from 30 to 300 microns, more preferably from 40 to 200 microns and most preferably from 70 to 100 microns.

5           The ability of the protective layer to elongate or stretch partially governs the elongation of the decorative protective film of the present invention. It is therefore preferred that the protective layer has an elongation of at least 30% at 40°C and of less than 400% at 60°C. Elongation is determined after the decorative protective film has been left for 10 minutes at a given temperature under a tension of 9.8 N/25mm. Generally, the ability of the decorative protective film to conform to a curved or complex-shaped surface is somewhat  
10           decreased when the elongation at 40°C is less than 30%. If the elongation at 60°C is more than 400% at 60°C, the decorative protective film may deform or even break when it is shaped, stretched or conformed over a curved or complex-shaped surface at a relatively high temperature immediately after heating. Preferably the decorative protective film preferably  
15           has an elongation of at least 33% at 40°C and an elongation of less than 350% at 60°C.

At 50°C, the protective layer preferably has an elongation of 100 to 350%, and preferably an elongation of 150 to 300%.

The protective layer has a tensile modulus of from 400 to 1300 MPa as measured by ASTM D638. More preferably, the tensile modulus of the protective layer is from 500 to  
20           1100 MPa and most preferably from 600 to 1000 MPa. If the protective layer has a tensile modulus of less than 400 MPa, continuous load can damage the protective layer when in combination with the toughening layers of the invention. A continuous load can deform or even tear the laminate film (wherein the laminate film comprises the protective layer and the toughening layer). If the tensile modulus of the protective layer is above 1300MPa, then  
25           generally it will be too difficult to apply the decorative protective film or laminate film over a three dimensional complex surface or a three-dimensional curved surface using a hand-held hot air blower.

The protective layer may be subjected to techniques of embossing or calendaring to enhance design properties, as long as it does not adversely affect the on the technical effects

of the present invention. Embossing gives some protrusions on the surface and a combination of the protrusions and the portions around the protrusion can create a three-dimensional appearance to the decorative finish. Calendering makes the protective layer smooth to reduce surface roughness, and can impart a high specular gloss giving a very glossy appearance.

5 Other finishes may be contemplated such as snakeskin, leather-appearance, patterns to reduce gloss etc.

#### Polyester resin composition

10 The protective layer is formed from a resin composition that contains a thermoplastic amorphous polyester resin, wherein the resin composition has a glass transition temperature of 20 to 60°C, a tensile modulus of 400-1300 MPa and excellent transparency.

The amorphous polyester resin composition may contain (i) a phthalate type polyester resin, such as polyethylene terephthalate, polybutylene terephthalate, polyethylene naphthalate and the like; and (ii) a polyether compound that is at least partially compatible  
15 with the phthalate type polyester resin. In this combination, the phthalate type polyester resin behaves as a thermoplastic resin and the polyether compound behaves as a plasticizer or softening agent. The combination has a large elongation even at a relatively low temperature and exhibits good toughness even at relatively high temperature. The amorphous resin composition provides shape compatibility to a curved surface when the decorative protective  
20 film is adhered by hand at a temperature of 40 to 60°C.

The phthalate type polyester resin is a polyester that has in one molecule both (a) a repeat unit derived from phthalic acid or naphthalic acid, such as terephthalic acid, isophthalic acid or naphthalic acid, and (b) a repeat unit derived from a diol. The polyester can be prepared by reacting a dicarboxylic acid or acid anhydride (e.g. phthalic acid or phthalic  
25 anhydride) and a diol by condensation polymerization.

The diols can be a mixture of (b-1) a linear aliphatic diol, such as ethylene glycol, butan-1,4-diol, hexan-1,6-diol, caprolactone diol and the like; and (b-2) an alicyclic diol, such as 1,4-cyclohexane methandiol, cyclohexane diol and the like. The amorphous polyester is preferably prepared from the diol mixture as mentioned above. The amorphous polyester

resin can easily give shape compatibility to a curved surface when the decorative protective film is adhered by hand at a temperature of 40 to 60°C.

It is preferred for the amorphous polyester resin of the present invention that a weight ratio of diols i.e. (b-1):(b-2), is 10:60 to 80:20.

5       The dicarboxylic acid or its derivative can be those other than phthalic acid. The amorphous polyester resin preferably has a number average molecular weight of at least 10,000, more preferably of 15,000 to 1,000,000.

The amorphous polyester sheets and webs are commercially available, such as Easter PETG polyester, available from Eastman Kodak Co. and the like.

10       The polyether compound can be an alkylene glycol type ether compound which contains a repeating unit of alkylene glycol having 2 to 6 carbon atoms. The alkylene glycol type ether compound includes 1) a polyalkylene glycol diether obtained by alkyl-etherifying both ends of a polyalkylene glycol (e.g. polyethylene glycol or tetramethylene glycol), or 2) a polyester ether having both alkylene glycol units and a dicarboxylic acid unit. The alkyl  
15       group for etherifying preferably includes a lower alkyl group (having not more than 3 carbon atoms), such as methyl group, ethyl group or a propyl group. Examples of dicarboxylic acids for 2) include aromatic dicarboxylic acids, such as terephthalic acid, isophthalic acid, phthalic acid, 2,6-naphthalene dicarboxylic acid, 1,5-naphthalene dicarboxylic acid and the like.

20       The polyalkylene glycol unit of the polyether compound is preferably a polyethylene glycol unit, which can produce a polymer having a large elongation even at a relatively low temperature and having good toughness even at a relatively high temperature.

25       The polyether compound generally has a number average molecular weight of 400 to 6,000, preferably 450 to 3,000, more preferably 500 to 3,000. Molecular weights more than 6,000 reduce an elongation of the resin composition at low temperatures and molecular weights of less than 400 reduce the toughness of the resin composition at higher temperatures.

30       The polyether compound may generally have a melting point of 150 to 250°C, a melt viscosity of 500 to 30,000 poise when determined at a shear rate of 100 sec<sup>-1</sup> and at a temperature of 250°C. Within the above range, the polyester resin composition can be formed into film by a conventional film-forming method, such as extruding or extrusion coating to easily obtain a polyester film for use as the protective layer. The polyether compound

preferably has a glass transition temperature  $T_g$  (as measured by peak temperature of  $\tan \delta$ ) of -50 to 30°C, more preferably -40 to 25°C, most preferably -30 to 20°C.

The polyether compound is commercially available under the trade names, such as BUTYCEL, BUTYCENOL, KYOWANOL, and the like.

5 The polyester resin composition may contain other additives, in addition to the essential components (i.e. thermoplastic polyester resin and polyether compound), so long as the additive or additives do not excessively deteriorate the transparency or the heat extensibility of the decorative protective sheet of the invention. Other additives that can be contained within the protective layer include but are not limited to colorants (such as dyes or  
10 pigments), plasticizers, softening agents, surfactants, fillers (including glass beads or ceramic beads and inorganic powders and minerals), crosslinking agents, flame retardants, ultraviolet absorbers, hindered amine light stabilizers, oxidation stabilizers, anti-fungal agents and the like. The protective layer preferably contains additives in an amount not exceeding 20 parts by weight of all additives per 100 parts by weight of the essential components (polyester and  
15 polyether).

#### Toughening layer

The toughening layer of the present invention may be one of (1) a resin layer containing colorant and thermoplastic resin, and (2) a polyurethane resin layer and at least one  
20 printing layer disposed on the resin layer and (3) a resin layer containing a colorant, a thermoplastic resin and at least one printed layer. When a printing layer is used to color the toughening layer, the printing layer is generally a layer of printing on the second or first surfaces (or both major surfaces) of the toughening layer. For example, the printing layer can provide a continuous color or a provide opacity and hiding power or both opacity and color.  
25 For these purposes, the printing layer is generally a continuous layer covering the whole of the first or second surfaces (both major surfaces) of the toughening layer. When the printing layer is present between the protective layer and the toughening layer, in those areas where the printing layer is present, the second surface of the protective layer is bonded to the first surface of the toughening layer by means of the printing layer.

Another type of printing layer can be a layer printed on the first major surface of the toughening layer which forms a design. In this case, the printing layer does not necessarily cover the whole of the first surface of the toughening layer, and the printing layer defines the decorative interface when the second surface of the protective layer is bonded to the first surface of the toughening layer. Printing the printing layer (the printing step) may be carried out by electrostatic printing, gravure printing, screen printing, inkjet printing and the like; and the resin layer can be one that has high affinity with ink or toner for printing.

The second surface of the toughening layer may have an optional adhesive prime layer to enhance adhesive power with the adhesive layer.

The toughening layer may be prepared by preparing a toughening layer coating liquid containing thermoplastic resin such as a polyurethane resin as the main component and coating and hardening (drying or curing) it. The toughening layer coating liquid contains a thermoplastic resin such as a polyurethane and is either melted to give the coating liquid for the toughening layer, or mixed with a solvent to give a liquid mixture which can then be coated. It is preferred that the toughening layer is colored, when this is the case the coating liquid comprises both a thermoplastic resin and a colorant. Preferably, the thermoplastic resin comprises a polyurethane and the colorant comprises a pigment. Coating can be conducted by a notch bar (knife edge), wire-wrapped bar, a round bar, extrusion coating, meter roll coating, slot dye coating or the like as is well known in the coatings industry. The toughening layer may also be formed by melt-extruding a material containing a film-forming polymer. Typically, the toughening layer coating liquid (e.g. melt, solution, dispersion, emulsion or the like) is coated onto a temporary support sheet. This yields a supported toughening layer comprising the toughening layer and the temporary support for the toughening layer wherein the second surface of the toughening layer is in contact with (and lightly adhered to) one major surface of the temporary support.

The thermoplastic resin for the toughening layer is preferably a polyurethane having a glass transition from -50°C to 0°C. The thermoplastic polyurethane resin preferably has a light transmittance of not less than 60%, more preferably not less than 70%. When a thermoplastic polyurethane is used having a glass transition temperature in this range, the toughening layer in combination with the protective layer (herein referred to as the laminate



film) has a high degree of flexibility. The toughening layer also imparts toughness to the protective layer, improving the impact resistance of the decorative film. It has been determined using Gardner impact tests (907g load), that without the toughening layer, the protective layer formed from amorphous thermoplastic polyester is more easily torn in use as furniture covering by impact from objects. For example, if used as a protective film for a desk or cushion, sliding of other furniture into the protective film causes tears to appear in the film, degrading the appearance and with holes, the protective film no longer protects the article to which it has been applied. So the use of a toughening layer comprising a polyurethane resin having a Tg from -50°C to 0°C increases the impact and tear resistance of the laminate film without unacceptably reducing the conformability or flexibility of the laminate film.

When the toughening layer contains a pigment as colorant, the toughening layer is said to be pigmented. Preferred pigments for use in the toughening layer include quinacridone pigments, isoindolinone pigments, carbon black, titanium dioxide, silica, talc, calcium carbonate and copper phthalocyanin pigments. The pigment can supply color to the decorative protective film or provide hiding power. Hiding power means that when the decorative protective film of the invention is applied to the surface of an article having a patterned surface, the hiding power is a measure of how well the decorative protective film can cover up patterns underneath it so that they are not well discerned by a human observer. If the underlying article surface has regular patterns - especially high contrast patterns (such as black and white patterns) these can be hard to cover up. The pigment desirably imparts a good degree of opacity to the polyurethane toughening layer.

The toughening layer may further contain an additives in addition to the thermoplastic polyurethane resin and an optional colorant. The additive may include metal gloss particles, plasticizers, softening agents, surfactants, fillers (including glass beads or ceramic beads and inorganic powders such as carbon black or silica), crosslinking agents, flame retardants, ultraviolet absorbers, hindered amine light stabilizers, oxidation stabilizers, antifungal agents and the like. Preferably the toughening layer contains a total amount of additives in an amount not exceeding 30 parts by weight per 100 parts by weight of the thermoplastic polyurethane resin.

The toughening layer preferably has good elongation for easy operation of adhering. The thickness of the toughening layer is from 10 $\mu$ m to 400  $\mu$ m and preferably from 15 to 200  $\mu$ m.

The toughening layer comprises a polyurethane resin having a glass transition temperature (T<sub>g</sub>) of from -50°C to 0°C as measured by Differential Scanning Calorimetry (D.S.C.), at a temperature ramp rate of 5°C/minute and at 62.8 rad/sec.

#### Adhesive layer

The adhesive layer generally contains adhesive polymer. The adhesive polymer may include acrylic polymers, silicone polymers,  $\alpha$ -polyolefin polymers, rubber polymers (e.g. synthetic rubber, such as styrene-butadiene-styrene SBS etc. or natural-rubber based polymers), polyurethane polymers or the like. Acrylic polymers are defined herein include polymers and copolymers of acrylic acid, methacrylic acid and esters thereof. An acrylic pressure sensitive adhesive layer is a layer of pressure sensitive adhesive comprising one or more acrylic polymers. The adhesive polymers may be used alone or in combination. The adhesive polymers may be prepared by polymerizing a monomer mixture containing suitable monomers. Polymerization can be conducted by a conventional method, such as solution polymerization, bulk polymerization, emulsion polymerization or the like.

The acrylic adhesive polymer may generally be prepared by polymerizing a monomer mixture of (A) an alkyl acrylate having 4 to 8 carbon atoms and (B) an (meth)acrylic acid monomer having a carboxylic group in a molecule. Another monomer to be copolymerized with the above two monomers, such as (meth)acrylic monomer and a vinyl-group containing monomer can also be used.

Examples of the monomer (A) are n-butyl acrylate, isobutyl acrylate, isooctyl acrylate, 2-ethylhexyl acrylate, and the like. Examples of the monomer (B) are (meth)acrylic acid. Examples of other monomers that may be used include phenoxyethyl acrylate, phenoxypropyl acrylate, 2-hydroxyethyl (meth)acrylate, 2-hydroxypropyl (meth)acrylate, 2-hydroxymethyl (meth)acrylate, hydroxy-3-phenoxypropyl acrylate, glycidyl (meth)acrylate, acryloyl benzophenone and the like.

The adhesive polymer is typically crosslinked. The crosslinking may be conducted by reacting a crosslinking agent with the polymer. Suitable crosslinking agents can include but are not limited to isocyanate compounds, epoxy compounds, bis-amide compounds, aziridines and the like. The amount of crosslinking agent in the adhesive layer is usually 0.1 to 5 parts by weight per 100 parts by weight of the adhesive polymer.

The adhesive layer may contain elastic microspheres or crystalline polymers, so long as they do not adversely affect the technical effects of the present invention. The adhesive layer may comprise a repositionable adhesive, a removable adhesive, positionable adhesives and permanent adhesives. The adhesive layer typically has a thickness of 5 to 200  $\mu\text{m}$ , preferably 10 to 100  $\mu\text{m}$ , as long as the purpose of the present invention can be attained.

Adhesives can also be selected by a variety of conventional adhesive formulations. Non-limiting examples of adhesives include pressure sensitive adhesives, hot melt adhesives, heat activated adhesives that are pressure sensitive adhesives at the time of application. Some suitable adhesives are disclosed in US Patents 4,994,322; 4,968,562; 5,296,277; 5,362,516 and 5,141,790 the entire disclosures of which are incorporated herein by reference. These references disclose both adhesive compositions and adhesive structures and associated release liners useful in the invention. Other types of adhesive include pressure sensitive adhesives disclosed in Satas et al. Handbook of Pressure Sensitive Adhesives, 2<sup>nd</sup> Edition (Von Nostrand Reinhold, N.Y., 1989). The layer of adhesive can cover all or part of the second surface of the toughening layer.

#### Primer layer

A primer layer is optional, as good adhesion can be obtained between an amorphous polyester protective layer and a polyurethane layer depending on the exact materials used. A primer layer may be fixedly disposed either on the first surface of the toughening layer or on the second surface of the protective layer. The primer layer may be formed from a primer polymer which is selected from a polymer having affinity with both the toughening layer and the protective layer. The primer polymer may comprise a vinyl acetate copolymer, a urethane elastomer or an (meth)acrylic polymer. The presence of the primer layer may increase adhesion between the protective layer and the toughening layer.

In addition, the urethane elastomer can be an elastomer formed from a polyurethane obtained by polymerizing a starting mixture containing a polyol and a diisocyanate.

The primer layer has a thickness of 0.1 to 30  $\mu\text{m}$ , preferably 0.5 to 10  $\mu\text{m}$ . Also, the primer layer may have a light transmittance of not less than 80%, preferably not less than 85%.

The primer layer may be formed by coating a solution containing the primer polymer on the toughening layer (or protective layer, and hardening by curing or drying). Coating may be done using coating methods known in the art such as a gravure coating, a bar coating (such as notch bar or knife edge, wire-wrapped bar and other similar metering methods), a roll coater such as meter roll coating, a die coater or the like.

#### Release liner

The optional release liner comprises a base and a release layer. Typically the release layer will be a silicone release layer. The base can comprise paper, plastic, plastic-coated paper, or a film-forming layer.

The free surface of the base defines the second surface of the release liner, and free surface of the release layer defines the first surface of the release liner (also called the release surface of the release liner).

The first surface of the release liner may be substantially flat or have an embossed or otherwise structured surface. The structured surface may be formed by embossing, hardening the release layer in contact with a structured surface, heat and pressure or other methods. Structured release liners, structured adhesive layers and methods for making and using them are known in the art. References that disclose release liners or adhesive layers or both include US Patent Application Publication Numbers 03-0017291-A1, 03-0178124-A1, 03-0152695-A1 03-0082371-A1; and US Patents 6,524,649, 6,524,675, 6,197,397, 5,650,215, 6,440,880, 6,123,890, 5,449,540 and 5,449,540 all of which are incorporated wherein by reference. Other references that disclose release liners include copending applications S/Ns 10/610005, 10/621658.

### Method of forming a decorative protective film

Herein extrusion generally refers to forcing a molten liquid at elevated temperatures through a die or dies into a nip and cooling the molten liquid (melt) to form a self-supporting sheet. Extrusion coating is defined as coating a molten liquid onto a support and allowing the liquid to cool and thereby harden (turn from a liquid greatly increase the viscosity of the liquid) by cooling to ambient temperatures.

Coating is defined herein as forming a layer of a coating liquid on a web or sheet of base material. When the coating liquid is a molten liquid (a melt), then hardening comprises cooling the layer of the coating liquid so that the layer either hardens to a solid or increases greatly in viscosity. When the coating liquid is a solution, emulsion or dispersion, then hardening the coating liquid comprises the step of drying the coating, i.e. heating the layer of coating liquid to drive off the solvent (e.g. an organic solvent or water) thus producing a dried coating. When the coating liquid is a liquid mixture at ambient temperature containing reactive diluents, then the step of hardening the liquid coating layer comprises the step of causing the reactive diluent to react with other components in the mixture to harden the coating layer. This can for example be accomplished by heating the coating, irradiating the coating with actinic radiation, or simply waiting (if for example the reactive diluent is introduced into the coating liquid at the coating head). Therefore depending on the nature of the coating liquid, hardening can be drying, solidifying, crosslinking or curing or any combination of one or more of these processes.

The polyester resin composition for the protective layer can be formed into a polyester film by any conventional film-forming method. The film-forming method of the polyester resin may include extrusion, extrusion coating onto a temporary support, extrusion by the T-die method, the blown film method, calendering, casting, coating onto a support or the like.

The polyester film used for the protective layer may be prepared as follows. An amorphous copolyester resin is mixed with a polyether compound in a particular weight-ratio and, if necessary, dried at 100 to 150°C for several hours to 10 hours to obtain a starting mixture. The starting mixture is put into an extruder and extruded at a particular temperature, generally 180 to 280°C and a particular extrusion-die temperature, generally 180 to 260°C

and then quenched by a casting roller to form a polyester film. The polyester film is a non-extended film, but if necessary, it may be monoaxially or biaxially oriented.

The ratio by weight of the amorphous copolyester resin to the polyether compound is preferably within the range of 70:30 to 99:1, more preferably in the range of 80:20 to 97:3, and most preferably in the range 85:15 to 95:5. If amorphous copolyester resin content is too high, the protective layer exhibits a reduced elongation at a lower temperatures. It the polyether content of the mixture is too high, the resultant protective layer is not sufficiently tough at higher temperatures.

Applying the toughening layer to a major surface of the protective layer may be accomplished as follows. The second surface of the polyester film is heat laminated with pressure to the first surface of the toughening layer. Any temporary support for the toughening layer is stripped off the second surface of the toughening layer to yield a laminate film. The laminate film comprises the protective layer and the toughening layer, wherein the second surface of the protective layer is bonded to the first surface of the toughening layer.

In another method of applying the toughening layer to the protective layer, the polyurethane-based toughening layer may be applied to the protective layer by coating a toughening layer coating liquid onto the second surface of the protective layer, and hardening the toughening layer to produce a laminate film. The laminate film comprises the protective layer and the toughening layer. The toughening layer coating liquid may be an emulsion, dispersion, solution, suspension or other type of coating liquid containing the components of the toughening layer. For example, the toughening layer coating liquid could contain an aqueous dispersion of the polyurethane resin component of the toughening layer with a dispersion of colorants and other additives. It is important that the toughening layer coating liquid does not dissolve or otherwise damage the protective layer onto which it is coated.

An adhesive layer may be applied to the second surface of the toughening layer to form a decorative protective film of the present invention. The adhesive layer may be applied to the second surface of the toughening layer by preparing a coating liquid containing adhesive polymer and then coating the adhesive coating liquid directly onto the second surface of the toughening layer. The liquid adhesive layer is then hardened, and then a release liner may optionally be laminated to the second surface of the adhesive layer (the free surface

of the adhesive layer not in contact with the toughening layer. Alternatively, a commercially-available adhesive layer may also be used.

An adhesive layer may also be applied to the second surface of the toughening layer as follows: The adhesive layer is formed by coating the adhesive coating liquid onto a temporary support such as a release liner and then hardening the liquid adhesive layer to give a supported adhesive layer. The supported adhesive layer comprises an adhesive layer and a release liner wherein the second surface of the adhesive is in contact with and lightly adhered to the release layer of the release liner and the other major surface of the adhesive layer is herein defined as the first major surface of the adhesive layer. The first surface of the adhesive layer of the supported adhesive layer is laminated to the second surface of the toughening layer (this step is a method of applying the adhesive layer to the second surface of the toughening layer) to give a decorative protective sheet. When the adhesive layer is a pressure sensitive adhesive layer, the lamination step is carried out under pressure and can be carried out at ambient temperatures without extra heating. When the adhesive layer is a hot-melt adhesive layer, then the lamination step is usually carried out with heat and pressure at elevated temperatures. Lamination typically involves pressing two (or more) layers together in pair of rollers in contact with each other where the point of contact of the rollers defines a nip as is known in the art. Other methods are possible.

Coating the adhesive layer can be accomplished by several methods. The adhesive layer may be coated out of a solvent such as water or an organic solvent. When the adhesive layer is coated out of a solvent, an adhesive polymer is mixed with the solvent and any other ingredients such as tackifiers, crosslinking agents etc. to form a coating liquid. The coating liquid can comprise a solution of the adhesive polymer in the solvent, a dispersion of the adhesive polymer in the solvent, an emulsion of the polymer in the solvent, a suspension of the polymer in the solvent, or other type of mixture of the adhesive polymer with the solvent. Organic solvents can include but are not limited to methyl ethyl ketone, methyl isobutyl ketone, ethanol, isopropanol, toluene or a mixture of two or more thereof. The adhesive layer is then hardened by the drying adhesive layer by evaporating the solvent.

Some pressure sensitive adhesive layers and most hot-melt adhesive layers may be hot-melt coated. In this case, one or more adhesive polymers is/are melted, mixed with other

ingredients and extrusion coated (or alternatively extruded). Hardening comprises the step of cooling the molten adhesive layer to ambient temperature. There may be other steps in the coating of the adhesive layer such as irradiating the adhesive layer.

5 The decorative protective film of the invention may have a decorated finish. The decorated finish is made by a method comprising the step of decorating the first surface of the protective layer (or by decorating both the first and second surfaces of the protective layer). Decorating a design or pattern can comprise printing, embossing, etching, engraving or otherwise forming a design or pattern.

10 Decorating the protective layer of the film can be done in several ways. When the protective layer is a self-supporting film, the first (or first and second) surface(s) may be decorated before the protective layer is bonded to the toughening layer. The first surface of the protective layer may also be decorated after the protective layer and the toughening layer are bonded together (wherein the second surface of the protective layer is bonded to the first surface of the toughening layer). The first surface of the protective layer of the decorative  
15 protective film may also be decorated when the decorative protective film comprises the protective layer, toughening layer and adhesive layer (with or without release liner).

An embossed design or pattern can be accomplished in several ways. When the protective layer is a self-supporting film, the first surface of the protective layer can be decorated by providing the protective layer, and embossing the first surface (or both major  
20 surfaces) of the protective layer. This can be accomplished by feeding the protective layer through a heated nip, where the nip comprises a roller having an embossed or engraved or etched surface, and a second roller (normally made of an elastic material such as rubber). Other methods are possible such as flat bed pressure. One or more of the rollers in this process are heated to help soften the protective layer and facilitate the embossing process. In  
25 order to prevent sticking of the protective layer onto a heated embossing roll, preferred roll temperatures are 60-70°C.

Other methods of decorating the first surface of the protective layer include gravure printing, inkjet printing, engraving, etching (dissolving portions of the surface), scratching, abrading screen printing, electrostatic printing, transferring pigment layers or layers  
30 comprising pigments etc.



Preferably the decorative protective layer of the invention comprising the protective layer, toughening layer and the adhesive layer but without a release liner has a thickness of less than 200 microns, more preferably less than 170 microns.

## 5     Methods of protecting an article

The decorative protective film of the invention may be applied to an article by removing the release liner (when present), applying the free (second surface) of the adhesive of the protective film to a surface of an article (the surface which it is desired to protect) and heating the film (for example with a hand-held hot air blower) and smoothing the film down  
10     to remove trapped air bubbles. During this process the film may be stretched over protrusions (so long as the protrusions are not sharp), wrapped around edges, butted up against edges and otherwise molded to the surface to be protected. This process where air bubbles are removed by smoothing the film onto a surface and the film is molded to the shape of the surface which it is to protect is herein referred to as conforming the film to a surface. The film may be  
15     smoothed by the hand or a squeegee or flat edge, a sponge or other known method.

Another method of protecting an article comprises the steps of providing a laminate film, wherein the laminate film comprises a protective layer and a toughening layer, applying an adhesive layer to an article to form an adhesive coated article, applying the second surface of the toughening layer of the laminate film to the adhesive layer, heating the laminate  
20     film and conforming the laminate film to the adhesive-coated article. In this case, the adhesive layer does not need to be a continuous adhesive layer. For example, the adhesive layer could be discontinuous or patchy or applied in stripes, dots, or other discontinuous patterns so long as the adhesive layer is sufficient to bond the laminate film (the toughening layer of the laminate film) to the article. For example, the adhesive layer could be applied to  
25     an article by spraying the adhesive onto one or more surfaces of an article. Alternatively, a double sided adhesive (a sheet both major surfaces of which are adhesive surfaces) could be applied to an article.

Articles for protection could include graphics, furniture such as desks, filing cabinets, desk sides and work surface tops, cushions, arms of chairs; building surfaces such as handrails  
30     for stairwells, doors, windows, escalator handrails, walls, drywall, concrete blocks, ceilings

and ceiling tiles; posters and poster board surfaces, foam core posters, Sintra board and other plastic display boards; boxes, cartons, chests and trunks.

### Examples

- 5           The present invention will be explained with reference to the following Examples.  
Unless otherwise stated, all percentages and ratios are by weight.

### Example 1

10           The protective layer was provided by using a 100  $\mu$ m thick amorphous thermoplastic polyester film available from Tatsuta Chemical (of Yanagibashi, Taito-ku, Tokyo, Japan) under the trade name of SCAT SP-044. The polyester film had a tensile modulus of approximately 1100MPa.

15           A 30% solution of polyurethane resin in a mixture of 5:2 methyl ethyl ketone (MEK) to methyl isobutyl ketone (MIBK) available as NIPPORAN YN-191 from Nippon Polyurethane Industry Co., Ltd. of Tokyo, Japan) was taken. The polyurethane solution (100 grams) was mixed with a pigment dispersion (ten grams) available as UTCO Series pigment dispersion (available from Dainichiseika Color & Chemicals Manufacturing Co., Ltd., of Tokyo, Japan). The UTCO Series dispersion contained black blue and silver-colored pigments and the concentration of the UTCO was less than 50% solids (weight per weight of dispersion). The mixture of the UTCO pigment dispersion and the NIPPORAN YN-191  
20           formed a toughening layer coating liquid (paint).

25           The toughening layer coating liquid was coated onto a temporary carrier (SCW2000 presized polyester available from 3M Company of Maplewood, Minnesota, USA) at a wet thickness of 100 microns by knife coating, and the liquid toughening layer was hardened by drying for two minutes at 150 °C. This formed a toughening layer on a temporary support, where the toughening layer had a free surface and a surface in contact with the support. The polyurethane of the toughening layer had a glass transition temperature of -2°C.

30           The free surface of the toughening layer was laminated to a major surface of the polyester film by passing through a heated nip (roll temperature was 200°C) which pressed the polyester film and the polyurethane layer together bonding the two together. The

temporary support was stripped off during this process giving a laminate film of the polyester layer and a colored polyurethane layer.

An acrylic adhesive layer was laminated to the free surface of the polyurethane layer of the laminate film obtained above by laminating by nip. The adhesive was an acrylic pressure sensitive adhesive on a liner. The dry thickness of the adhesive layer was approximately 43 microns thick. This gave a decorative protective film comprising a polyester layer as the protective layer, polyurethane layer as the toughening layer, an adhesive layer and a release liner.

#### Comparative Example 1

This was carried out in the same manner as Example 1, except that a different amorphous thermoplastic polyester was used available as SCAT SP-012 available from Tatsuta Chemical (of Yanagibashi, Taito-ku, Tokyo, Japan). The thickness of the polyester film was 100 $\mu$ m (as in Example 1) but the tensile modulus was lower at approximately 400 MPa.

#### Comparative Example 2

This was carried out in the same manner as Example 1 except that the polyurethane resin layer having a glass transition temperature of -2°C was replaced by an acrylic resin layer having a glass transition temperature of above 0°C. A different coating liquid was coated onto the temporary support in place of the polyurethane mixture used in Example 1. The coating liquid comprised a 30% solids solution of an acrylic resin, Paraloid B-48N (available from Rohm and Haas of Philadelphia, U.S.A.) in a solvent mixture of one part MEK, one part toluene and one part MIBK. This acrylic resin has a glass transition temperature of above 0°C. The acrylic layer was dried at 150°C for two minutes. The acrylic layer was laminated to the same polyester film as used in Example 1 in the same manner, and the temporary support removed to give a laminate film comprising a polyester layer and an acrylic layer. The same adhesive on a liner as was used in Example 1 was laminated to the free surface of the acrylic layer.

### Comparative Example 3

This was carried out as Example 1 except that the amorphous polyester film used had a different thickness (gauge), the thickness being 200 microns (also available as SCAT SP-044 from Tatsuda Chemical).

5

### TESTING

#### Test Method 1

Two samples of each decorative protective film from Example 1 and two samples of the film from Comparative Example 1 were taken, the release liner removed from the adhesive layer of each sample, and the decorative protective film samples applied to a 1 mm thick aluminum plate (the free adhesive surface was laminated onto the aluminum plate). A 3mm thick shock-absorbing material was placed over the film samples on the plate and a weight placed on top of each sample (on top of the shock absorbing material). Two different weights were used such that a pressure was applied to the film of  $50\text{g/cm}^2$  for one sample and  $100\text{g/cm}^2$  with the other sample. The samples were left under load in an oven at  $40^\circ\text{C}$  for one week.

10

15

Results are shown in TABLE 1.

TABLE 1		
Example >	Example 1	Comparative Example 1
Film >	Amorphous polyester 1100 MPa tensile modulus	Amorphous polyester - tensile modulus was less than 400 MPa
↓ Load		
50g/cm <sup>2</sup>	No damage observed	Surface of polyester film was damaged
100g/cm <sup>2</sup>	No damage observed	Surface of polyester film was damaged

#### Test Method 2

5

Samples of the film from Example 1 and from Comparative Example 2 were adhered to a 1 mm thick aluminum plate, and a Gardner Impact Resistance test (ASTM NUMBER OR JIS TEST NUMBER?) carried out at 5°C. Results are shown in TABLE 2.

TABLE 2								
Example	Energy/J							
	1.13	2.26	3.39	4.52	5.65	6.78	7.91	9.04
Example 1	O	O	O	O	O	O	O	O
Comparative Example 2	O	O	O	O	O	O	X	X
O = film not broken by impact								
X = film was broken by impact								

10

### Test Method 3

5 The heat release rate and total heat release of three film samples from Example 1 and three film samples from Comparative Example 3 were measured using a cone calorimeter (available from Fire Testing Technology of East Grinstead, West Sussex, U.K.). The specimen surface area was  $88.4 \text{ cm}^2$ , heat flux  $50 \text{ kW/m}^2$  and an exhaust duct flow rate of 24 liters/sec. The test results are shown in TABLE 3.

TABLE 3				
Example	Polyester layer thickness	Maximum Heat Release Rate (HRR) $\text{/kW-m}^{-2}$	Time exceeding $200 \text{ kW-m}^{-2}/\text{sec}$	Total Heat Released (THR) until Flameout $\text{/MJ-m}^{-2}$
Example 1	100 $\mu\text{m}$	265	10	3.90
		267	10	4.09
		278	10	3.98
Comparative Example 3	200 $\mu\text{m}$	336	14	6.08
		321	14	5.89
		332	14	6.29

We claim:

1. A decorative protective film, comprising:

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a protective layer having a first surface and a second surface, wherein the protective layer comprises an amorphous thermoplastic polyester resin, and wherein the polyester layer has a tensile modulus of from 400 to 1300 MPa;

10

a toughening layer having a first surface and a second surface, wherein the toughening layer comprises a polyurethane resin having a glass transition from -50°C to 0°C, and wherein the second surface of the protective layer is bonded to the first surface of the protective layer; and

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an adhesive layer having a first surface and a second surface, wherein the first surface of the adhesive layer is bonded to the second surface of the toughening layer.

2. The decorative protective film of claim 1, wherein the adhesive layer is an acrylic pressure sensitive adhesive layer.

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3. The decorative protective film of claim 1 or claim 2, further comprising a decorated interface between the protective layer and the toughening layer.

25

4. The decorative protective film of claim 1, wherein the first surface of the protective layer is decorated by a method selected from the group consisting of printing, embossing, and a combination of printing and embossing.

6. The decorative protective film of claim 1, wherein the toughening layer contains a pigment.

7. A decorated article, comprising:

a protective layer having a first surface and a second surface, wherein the protective layer comprises an amorphous thermoplastic polyester resin having a glass transition temperature of 20 to 60°C, and wherein the protective layer has a tensile modulus of 400-1300 MPa;

5 a toughening layer having a first surface and a second surface, wherein the toughening layer comprises a polyurethane resin having a glass transition from -50°C to 0°C, and wherein the second surface of the protective layer is bonded to the first surface of the toughening layer;

10 an adhesive layer having a first surface and a second surface, and wherein the first surface of the adhesive layer is bonded to the second surface of the toughening layer; and

an article having at least one major surface, wherein the second surface of the adhesive is adhered to the major surface of the article,

15 wherein the protective layer, toughening layer and adhesive layer together define a decorative protective film and wherein the decorative protective film is conformed to the major surface of the article.

8. The article of claim 7, wherein the toughening layer is pigmented.

9. A method of preparing a decorative protective film, comprising the steps of:

20 providing a protective layer, the protective layer comprising a layer of thermoplastic amorphous polyester having a tensile modulus of 400-1300 MPa;

applying a toughening layer to a major surface of the protective layer, wherein the toughening layer comprises a polyurethane resin having a glass transition temperature of -50° to 0°C; and

25 applying an adhesive layer to the second surface of the toughening layer.

10. The method of claim 9, further comprising the step of decorating the first surface of the protective layer.



11. The method of claim 10, wherein the step of decorating the protective layer comprises embossing the first surface of the protective layer.

11. The method of claim 9 further comprising the step of printing the toughening layer.

5

12. The method of claim 9 further comprising the step of printing the second surface of the protective layer.

13. A method of preparing a protected article, comprising the steps of:

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providing the decorative protective film of claim 1;  
applying the second surface of the adhesive layer to an article;  
heating the decorative protective film; and  
conforming the decorative film to the article.

15

14. A method of preparing an article comprising the steps of:

providing a film,  
applying an adhesive layer to an article to form an adhesive coated article;  
applying the film to the adhesive coated article;  
heating the film; and  
conforming the film to the adhesive coated article.

20

15. The method of claim 14, wherein the film is a laminate film and the laminate film comprises:

25

a protective layer having a first surface and a second surface, wherein the protective layer comprises an amorphous thermoplastic polyester resin, wherein the protective layer has a tensile modulus of from 400 to 1300 MPa;

a toughening layer having a first surface and a second surface, wherein the toughening layer comprises a polyurethane resin having a glass transition from -50°C to 0°C, and wherein the second surface of the protective layer is bonded to the first surface of the toughening layer;

30

and wherein applying the film to the adhesive coated article comprises the step of applying the second surface of the toughening layer to the adhesive coated article.

## Decorative protective film

### Abstract

5           The present invention provides a decorative protective film which can be adhered on a surface of an article having a three-dimensional curved surface, even when the operation is conducted in-situ at temperatures of 40 to 60 °C, and which does not comprise poly(vinyl chloride). The decorative protective film comprises in order; an embossable protective layer, a toughening layer bonded to one major surface of the protective layer, and an adhesive layer  
10       formed on the other surface of the toughening layer. The protective layer comprises a thermoplastic amorphous polyester resin having a tensile modulus of 400 to 1300 MPa. The toughening layer comprises a polyurethane resin having a glass transition temperature of -50°C to 0°C. The toughening layer is preferably colored and preferably contains one or more colorants such as pigments.

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